

Appendix Q

Ex Situ Grouting of Pad A Nitrate Salt Tests

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Appendix Q

Ex Situ Grouting of Pad A Nitrate Salt Tests

Ex situ grouting is being considered for treatment of the Pad A salt waste, which is stored on an asphalt pad on the ground surface at the Radioactive Waste Management Complex. Ex situ grouting includes selection of an appropriate grout and the design of an approach to transfer the waste from Pad A to a mixing system where existing containers could be opened, waste contents could be mixed with grout, and waste-grout mix could be placed into containers for disposal. This test only addresses grouting of Pad A waste.

Pad A waste consists of 30 wt% potassium nitrate and 60 wt% sodium nitrate flakes with about 400 ppm of soluble chromium (much as chromium plus six) and 180 pCi/g of uranium. Samples of Pad A waste were used in this mixing study (see Table A-2 in Appendix A).

Three candidate grouts were identified for Pad A ex situ testing: Polysiloxane, Saltstone, and WAXFIX. Dimethyl Polysiloxane, marketed by Technologies Vision Grout, used a polymer encapsulation technology shown to successfully encapsulate surrogate salt materials (Loomis, Miller, and Prewett 1997). Saltstone is a Portland-cement-based, blast-furnace-slag-based, and coal-fly-ash-based grout developed by Savannah River and is used for salt waste treatment (Franz 1985). WAXFIX, by Ernie Carter Technologies, consists of paraffin and proprietary fillers for encapsulation of solid waste (Loomis et al. 2003). The compositions for these grouts are noted in Table A-6 of Appendix A.

Q-1. TEST OBJECTIVES, RATIONALE, AND DEVIATIONS FROM TEST PLAN

The objectives for the solidification and stabilization tests of ex situ Pad A are (1) estimate the potential for the release of contaminants from the final waste form and (2) evaluate the durability of grout/salt waste forms. To meet these objectives, Yancey et al. (2003) called for two leach tests. The first test is the U.S. Environmental Protection Agency (EPA) toxicity characteristic leaching procedure (TCLP) to check for chromium retention in grouted specimens (EPA 1997). The second test, uranium stabilization, was measured through the standard, "Measurement of the Leachability of Solidified Low-Level Radioactivity Wastes by a Short-Term Test Procedure" (ANS 16.1). The waste loadings in the samples were 0, 25, and 50 wt% in accordance with Table 41 of Yancey et al. (2003).

Section 4.4.2.1 of Yancey et al. (2003) called for the grout to be sieved to a specific range (below a 9.4-mm [0.4-in.] sieve and above a 4.8-mm [0.2-in.] sieve). The standard EPA TCLP requires that grout pieces of 9.5 mm (0.4 in.) and smaller be leached (no lower size limit imposed); the tests were done according to the standard EPA TCLP procedure.

Q-2. EXPERIMENTAL DESIGN AND PROCEDURES

As noted above, three types of grout methods were specified in Yancey et al. (2003). The Pad A material was to be grouted at 25 and 50 wt% loading in addition to a control or blank sample at 0 wt% loading. Triplicate samples of each were prepared for minimum statistical comparison. Following a minimum of 28 days of curing, the samples were subjected to the TCLP and American Nuclear Society (ANS) leach tests. In addition to the analyses specified in Yancey et al. (2003), nitrate also was measured in the ANS leachants. Since the Pad A waste is composed of about 60 wt% nitrate, a measure of the grout

stability is to determine the amount of nitrate that is leached into the groundwater. The leach solutions were analyzed by inductively coupled plasma-mass spectrometry for chromium and uranium and by ion selective electrode for nitrate.

For the ANS leach test, Yancey et al. (2003) specifies the use of simulated groundwater for the leach solution. The solution was used to represent the anticipated groundwater in the Subsurface Disposal Area. The simulated groundwater composition contained very low amounts of magnesium sulfate, calcium chloride, sodium nitrate, sodium bicarbonate, potassium bicarbonate, and potassium nitrate (see Table A-1 in Appendix A).

Q-3. EQUIPMENT AND MATERIALS

The Pad A waste sample was provided from the Radioactive Waste Management Complex (see Figure Q-1). The sample was analyzed by inductively coupled plasma-mass spectrometry for chromium and uranium and found to contain 349 ppm of chromium, 3.4 pCi/g of U-235, and 39.3 pCi/g of U-238. For this study, all leach results were in total uranium, and the calculations were based on U-238.

The WAXFIX and Polysiloxane grouts were provided by the vendors (see Table A-5 in Appendix A). The WAXFIX was heated to over 60°C (140°F), mixed with waste, placed in cylindrical molds, and allowed to cool. The Polysiloxane was provided as two components and prepared with 10 parts A to one part B. These were mixed together, and then the waste was added and placed in the molds.

The Saltstone grout is prepared locally from commercially available cement materials. It is mixed with 3.3 wt% of Portland cement, 27.7 wt% of blast furnace slag, 27.7 wt% of coal fly ash, and 41.3 wt% of water. There is a water-to-solid ratio of 7-to-10 for the Saltstone grout before waste addition. The grout was prepared as noted, the Pad A waste was added to meet the specified waste loading, and the grout was placed in the molds to cure. The Portland cement was ordinary Portland cement, ASTM C150, Type I/II. Blast furnace slag must meet ASTM C989, Grade 120, where the slag is finely ground to bring out the cementitious properties. Coal fly ash meets ASTM C618, Class F, which is the glassy fly ash.

The grout molds were prepared locally and designed specifically for the ANS test. The ANS test requires that the volume of leach water be 10 times the surface area of the specimen. Therefore, a smaller specimen is preferred to reduce the amount of low-level radioactive water for disposal. For this test, the specimens were conical frustums with a base diameter of 19 mm (0.75 in.), a top diameter of 18 mm (0.71 in.), and a height of 31 mm (1.2 in.). The slight change in diameter allows for the specimen to be extracted from the mold in the event that the grout expands during curing. The core of the mold is made from Teflon to also facilitate extraction. The base and top are Plexiglas. One end of a plastic beaded chain is placed in the grout. This chain suspends the specimen in the leach water during the ANS leach test and allows the specimen to be easily moved between successive leachants (see Figures Q-2 and Q-3). Vacuum grease is placed between the Teflon core and the Plexiglas base to prevent leakage of grout fluids. Rubber bands hold the mold parts together. The molds with the grouts are cured in sealed plastic bags for at least 28 days.

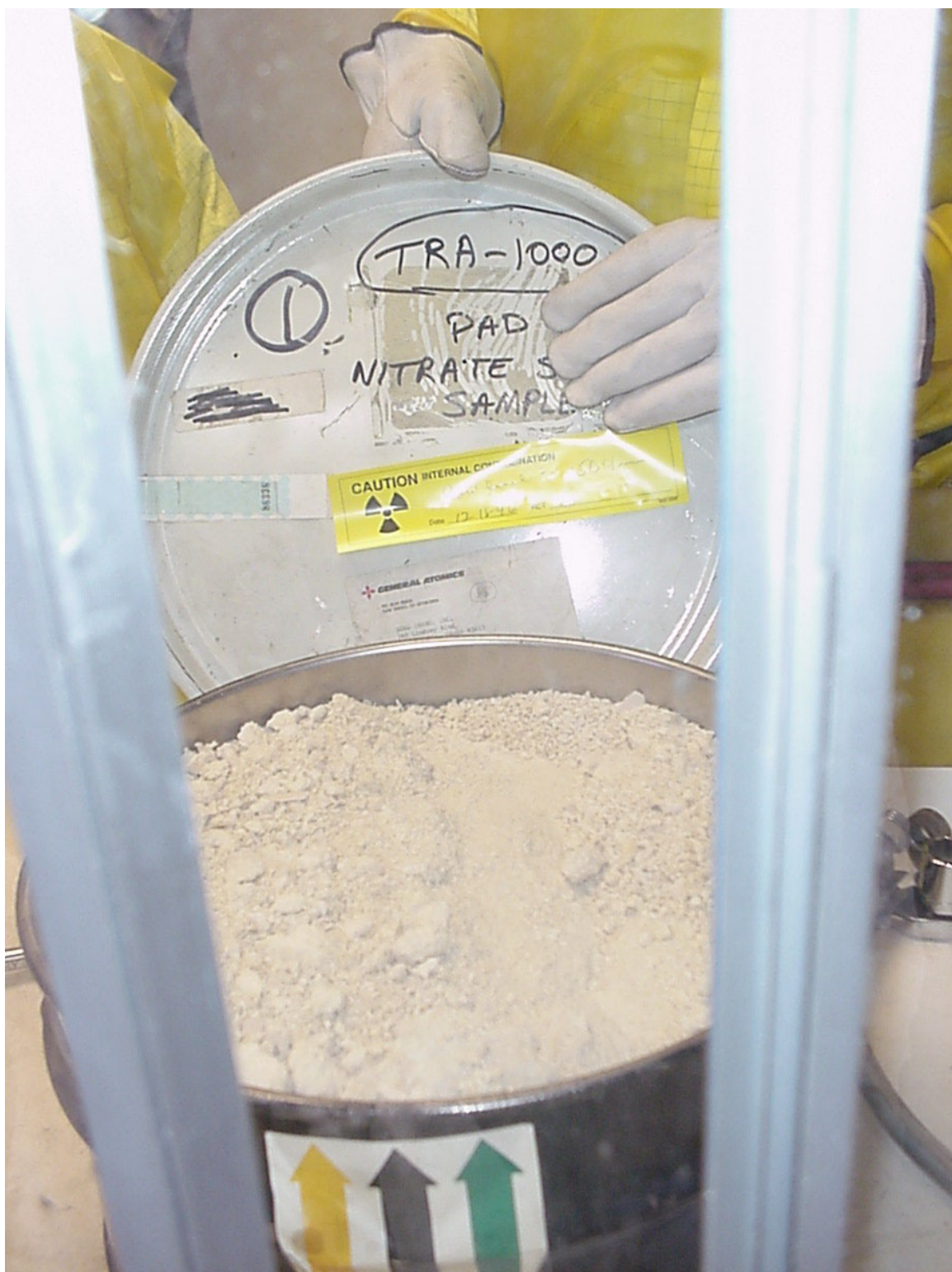


Figure Q-1. Pad A waste.

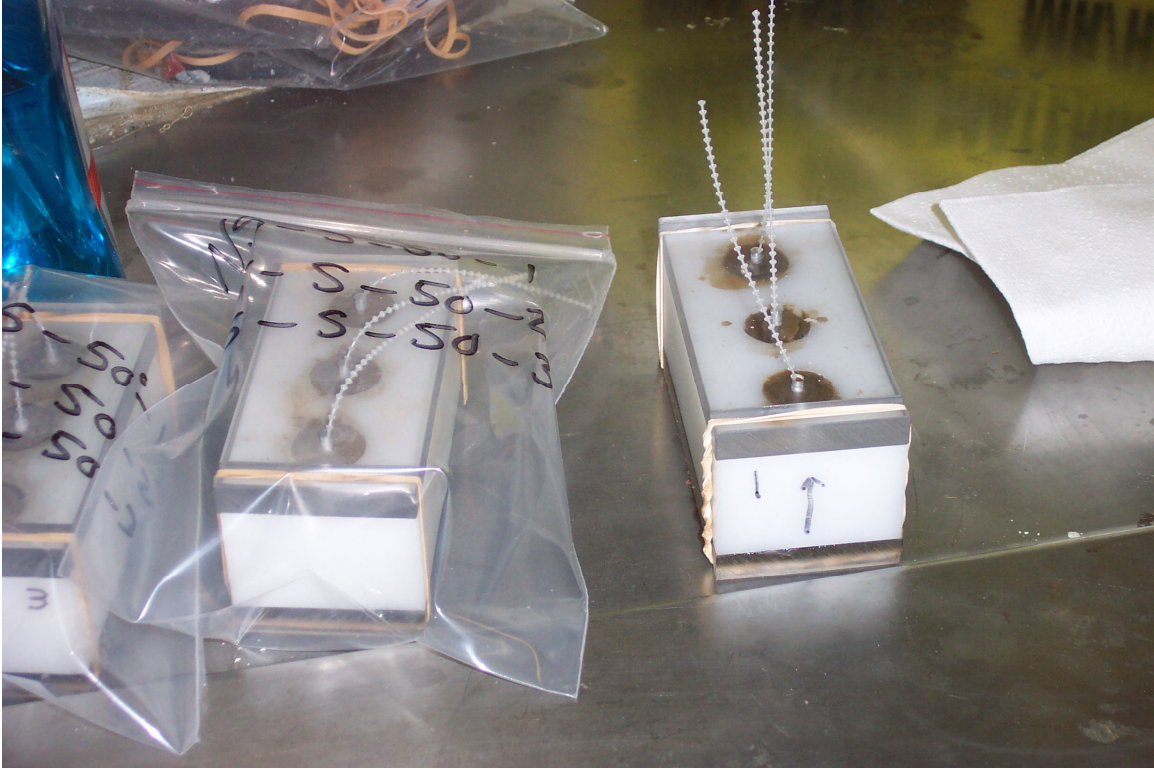


Figure Q-2. Specimen molds with beaded chains.



Figure Q-3. American Nuclear Society 16.1 leach test setup (WAXFIX samples in water).

Q-4. DATA MANAGEMENT, ANALYSIS, AND INTERPRETATION

This work was conducted to Quality Level 3 (i.e., standard laboratory practices with no specific calibrations to National Bureau of Standards). No chain of custody of samples was maintained; however, unique sample identifiers were used.

Solution pH was measured using an Orion pH meter (Model 420A) and standard pH probe with temperature compensation. A three-point calibration was completed before use with laboratory standard solutions at pH levels 4, 7, and 10.

Solution oxidation-reduction potential (ORP) was measured simultaneously with the pH on the Orion meter using an ORP (or redox) probe with the readout in millivolts. No calibration was made for this measurement; however, the data provide relative comparisons between grouts.

Leach solution nitrate concentration was measured also using the Orion meter with an ion-specific nitrate probe. For calibration, three nitrate standards were prepared using sodium nitrate in concentrations of 0.1 *M*, 0.001 *M*, and 0.00001 *M*. Millivolt readings were taken for each of these solutions and plotted on log-log graph paper. A straight line results that allows correlation of the millivolt reading to the nitrate molarity.

As noted earlier, triplicate samples were to be prepared for analysis. For each grout formulation, a common batch was prepared at the specified waste loading of 25 and 50 wt%. From the common mix, six specimens were made: three for TCLP and three for ANS leach testing. Therefore, the triplicate sets have a common basis before the analytical work. Also of note is that the waste-loading weight percent is calculated on the as-mixed or “wet” grout masses. Some moisture loss may occur during curing and is not accounted for in the mixture waste loading or in the as-mixed density.

The leach index values were calculated according to the ANS 16.1 procedure; a two-tailed student *t* test with a 99.9% confidence level was used. Based on the small number of replicates (three) and the complexity of the grout and waste systems being studied, a two-tailed student *t* with a 95% confidence level was selected for statistical comparison (where appropriate) of the remaining data.

Q-5. RESULTS AND CONCLUSIONS

The Saltstone, WAXFIX, and Polysiloxane grouts were prepared at 0, 25, and 50 wt% waste loading as noted in Tables Q-1–Q-3. Following at least 28 days of curing, the waste form specimens were removed from the molds and submitted for TCLP and ANS testing. Figures Q-4 through Q-9 show photographs of test samples of Polysiloxane, Saltstone, and WAXFIX that contain Pad A nitrate salt waste. The sections below describe the results, observations, and conclusions for each test and each waste form.

Table Q-1. Grout formulations—Saltstone.

Waste Form	Pad A Waste (wt%)	Water (wt%)	Cement (wt%)	Slag (wt%)	Fly Ash (wt%)	Mix Density (g/cm ³)
Saltstone control	0	41.3	3.3	27.7	27.7	1.59
Saltstone 25 wt%	25.0	31.0	2.6	20.7	20.7	1.46
Saltstone 50 wt%	50.0	20.7	1.7	13.8	13.8	1.64

Table Q-2. Grout formulations—WAXFIX.

Waste Form	Pad A Waste (wt%)	WAXFIX (wt%)	Mix Density (g/cm ³)
WAXFIX control	0	100	0.90
WAXFIX 25 wt%	25	75	1.12
WAXFIX 50 wt%	50	50	1.22

Table Q-3. Grout formulations—Polysiloxane.

Waste Form	Pad A Waste (wt%)	Part A (wt%)	Part B (wt%)	Mix Density (g/cm ³)
Polysiloxane control	0	90.9	9.1	1.19
Polysiloxane 25 wt%	23.3	69.7	7.0	1.31
Polysiloxane 50 wt%	47.6	47.6	4.8	1.43

Q-5.1 Qualitative Observations

The Saltstone grouts were extremely fluid and resulted in bleed water on the surface of the waste form. In addition, the Saltstone 50 wt% formulation did not set up. The lack of proper curing is most likely from the very high nitrate concentration in the waste form at 50 wt% loading. Both the bleed water and the nonset can be resolved by reducing the water content and reducing the waste loading somewhere between the 25 and 50 wt%.

The Polysiloxane mixture was extremely viscous. The polymer by itself was quite thick, and the addition of the solid, dry waste made the mixture even thicker. This issue would need to be addressed in the type of mixer equipment selected. The final product was heterogeneous and, in nonscientific terms, looked like salami or sausage with the Polysiloxane being red with the white Pad A waste dispersed throughout polymer.

The WAXFIX, when melted, is very fluid and easily incorporated into the dry waste; however, when placed in the molds, the solid waste tends to settle to the bottom before the wax cools sufficiently to retard settling. Temperature control would need to be addressed when utilizing WAXFIX on a production basis in order to control waste-loading quality.

One other point to be noted is that the Polysiloxane 50-wt% Sample Number 2 (PP-A-50-2) was damaged (gouged) during extraction from the mold. This is thought to explain the larger standard deviations observed in that set of triplicate samples. Polysiloxane immobilizes contaminants by encapsulation. A damaged waste form can lead to additional leaching with encapsulated waste. As long as the encapsulation is intact, leaching is reduced; however, if the encapsulation is damaged, the waste is open to leaching.



Figure Q-4. Pad A waste in Polysiloxane at 25 wt% loading (post-American-Nuclear-Society leach).



Figure Q-5. Pad A waste in Polysiloxane at 50 wt% loading (post-American-Nuclear-Society leach).



Figure Q-6. Pad A waste in Saltstone at 25 wt% loading (post-American-Nuclear-Society leach).



Figure Q-7. Pad A waste in Saltstone at 50 wt% loading (post-American-Nuclear-Society leach).



Figure Q-8. Pad A waste in WAXFIX at 25 wt% loading (post-American-Nuclear-Society leach).



Figure Q-9. Pad A waste in WAXFIX at 50 wt% loading (post-American-Nuclear-Society leach).

Q-5.2 Toxicity Characteristic Leaching Procedure Results for Chromium

In each waste form and at all loading levels, chromium leached less than the toxicity characteristic level of 5.0 mg/L (EPA 268_40). Only the control (0 wt%) and the 25- and 50-wt% samples of Saltstone passed the universal treatment standard of 0.60 mg/L (EPA 268_48). Figure Q-10 summarizes the results (see Table Q-4 for details). It is noted that the Saltstone leach levels for the 25- and 50-wt% samples were less than the control sample. This may be because of the bleed water problem in that the chromium left the sample in the bleed water and was not present in the final grout subjected to TCLP. In testing the bleed water samples, chromium was found at 220 mg/L, which represents 16.8% of the chromium in the 25-wt% sample. For the 50-wt% sample, chromium was found at 577 mg/L, which is 7.7% of the chromium in the sample. Thus, a portion of the chromium is in the bleed water, but the majority is retained in the grout. However, any bleed water is well above the Resource Conservation and Recovery Act toxicity limit for chromium.

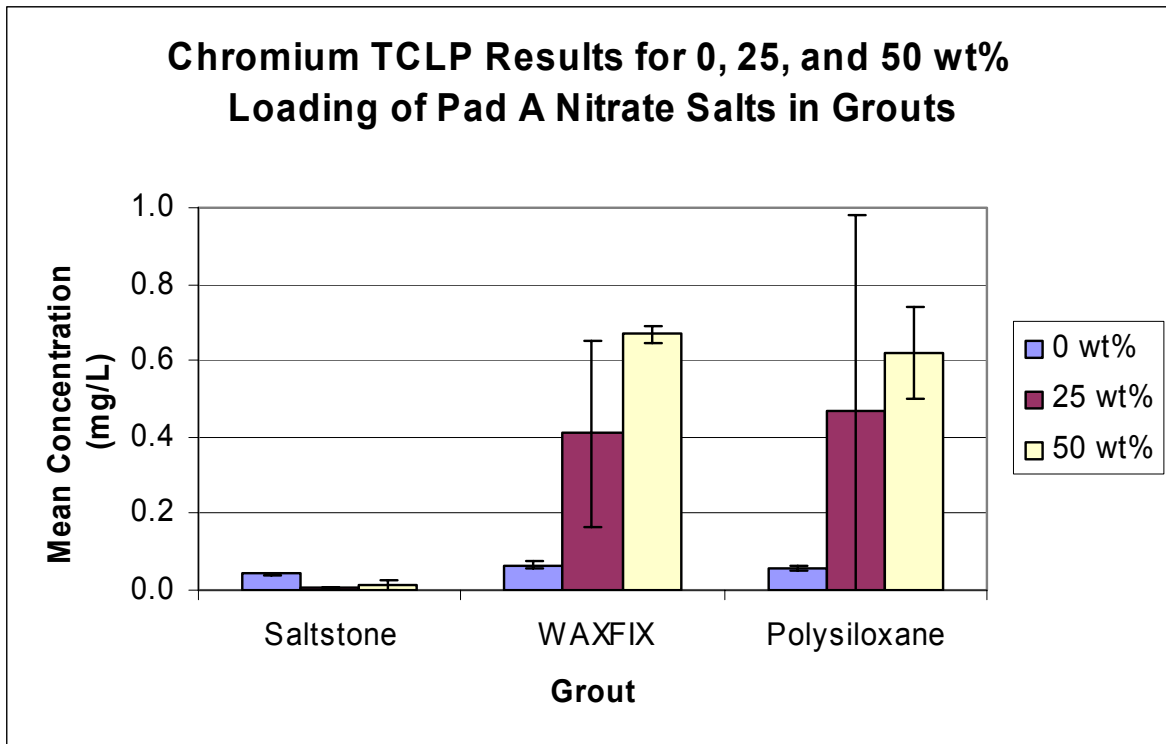


Figure Q-10. Toxicity characteristic leaching procedure results for chromium (the U.S. Environmental Protection Agency characteristic limit = 5.0 mg/L, and the universal treatment standard limit = 0.60 mg/L).

Table Q-4. Toxicity characteristic leaching procedure results for chromium (U.S. Environmental Protection Agency characteristic limit = 5.0 mg/L, and universal treatment standard limit = 0.60 mg/L).

Waste Form	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Mean (mg/L)	Standard Deviation	Confidence interval
Saltstone 0 wt% control	0.042	0.043	Not sampled	4.25E-02	7.07E-04	1.76E-03
Saltstone 25 wt%	0.006	0.006	0.005	5.67E-03	5.77E-04	1.43E-03
Saltstone 50 wt%	0.016	0.010	0.006	1.07E-02	5.03E-03	1.25E-02
WAXFIX 0 wt% control	0.065	0.070	0.061	6.53E-02	4.51E-03	1.12E-02
WAXFIX 25 wt%	0.519	0.376	0.330	4.08E-01	9.86E-02	2.45E-01
WAXFIX 50 wt%	0.660	0.666	0.679	6.68E-01	9.71E-03	2.41E-02
Polysiloxane 0 wt% control	0.058	0.053	0.056	5.57E-02	2.52E-03	6.25E-03
Polysiloxane 25 wt%	0.509	0.243	0.649	4.67E-01	2.06E-01	5.12E-01
Polysiloxane 50 wt%	0.564	0.649	0.649	6.21E-01	4.91E-02	1.22E-01

Q-5.3 American Nuclear Society 16.1 Leach Test Results for Uranium, Nitrate, pH, and Oxidation-Reduction Potential

The uranium concentration data, in parts per billion, from the leach test are presented in Figure Q-11 (see data in Table Q-5). The figure indicates that more of the uranium leached from the WAXFIX-50 and the Polysiloxane-50 samples than from the other samples. The time slots of 2 hours, 7 hours, 24 hours, 48 hours, 72 hours, 96 hours, and 120 hours correspond to leach intervals 1 through 7. It is noted that the majority of uranium in the 50-wt% WAXFIX and Polysiloxane samples leached out within the first 48 hours. The ANS leach test results and calculations produce a leach index for the radionuclide of interest, in this case, uranium. In all cases at all loadings, the waste form leach indices were greater than 6 as noted in Table Q-6 and Figure Q-12. Figure Q-13 shows the same data expressed as effective diffusivity. (Leach index is the log of the inverse of the effective diffusivity.) As effective diffusivity values increase (Figure Q-13), more of the element being measured is leached from the sample. A perfect diffusivity in this case would be zero. The table also notes that between 5% and 11% of uranium in the specimen leached. Table Q-6 gives the overall leach index, whereas the figures give the individual leach indices for each leach interval. Only the overall leach index is used to judge the quality of the waste form; however, the individual indices give an indication of when the uranium leached. Section Q6 provides a sample leach index calculation.

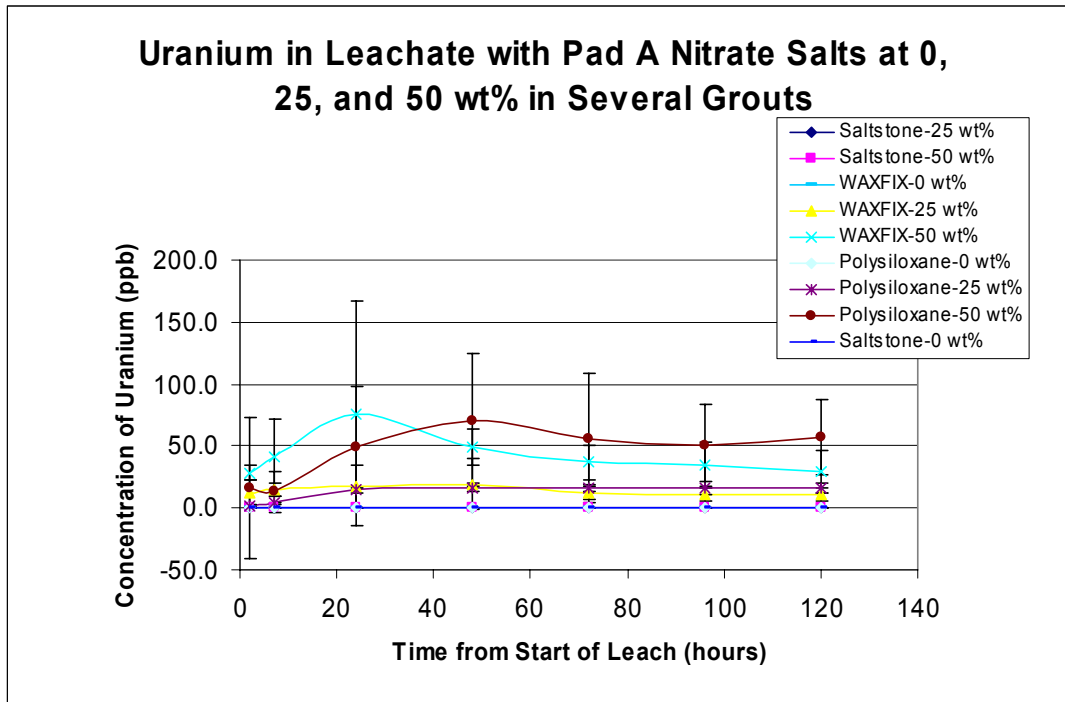


Figure Q-11. Uranium leach results.

Table Q-5. American Nuclear Society leach interval uranium results.

Sample	2 Hours Leach #1 (pCi/mL)	7 Hours Leach #2 (pCi/mL)	24 Hours Leach #3 (pCi/mL)	48 Hours Leach #4 (pCi/mL)	72 Hours Leach #5 (pCi/mL)	96 Hours Leach #6 (pCi/mL)	120 Hours Leach #7 (pCi/mL)
Saltstone 0 wt%							
Replicate 1	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05
Replicate 2	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05
Replicate 3	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05
Mean	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05
Standard deviation	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Confidence interval	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Saltstone 25 wt%							
Replicate 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Replicate 2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Replicate 3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mean	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Standard deviation	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Confidence interval	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Saltstone 50 wt%							
Replicate 1	3.36E-05	3.36E-05	6.72E-05	0.0	0.0	0.0	0.0
Replicate 2	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table Q-5. (continued).

Sample	2 Hours Leach #1 (pCi/mL)	7 Hours Leach #2 (pCi/mL)	24 Hours Leach #3 (pCi/mL)	48 Hours Leach #4 (pCi/mL)	72 Hours Leach #5 (pCi/mL)	96 Hours Leach #6 (pCi/mL)	120 Hours Leach #7 (pCi/mL)
Replicate 3	3.36E-05	0.0	0.0	0.0	0.0	0.0	0.0
Mean	2.24E-05	1.12E-05	2.24E-05	0.0	0.0	0.0	0.0
Standard deviation	1.94E-05	1.94E-05	3.88E-05	0.0	0.0	0.0	0.0
Confidence interval	4.82E-05	4.82E-05	9.64E-05	0.0	0.0	0.0	0.0
WAXFIX 0 wt%							
Replicate 1	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05
Replicate 2	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05
Replicate 3	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05
Mean	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05	3.36E-05
Standard deviation	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Confidence interval	0.0	0.0	0.0	0.0	0.0	0.0	0.0
WAXFIX 25 wt%							
Replicate 1	5.38E-03	5.38E-03	8.06E-03	7.39E-03	5.04E-03	3.70E-03	4.37E-03
Replicate 2	4.70E-03	4.03E-03	5.71E-03	3.36E-03	3.70E-03	3.02E-03	3.02E-03
Replicate 3	2.59E-03	5.38E-03	3.36E-03	8.74E-03	4.03E-03	4.37E-03	4.03E-03
Mean	4.22E-03	4.93E-03	5.71E-03	6.50E-03	4.26E-03	3.70E-03	3.81E-03
Standard deviation	1.46E-03	7.76E-04	2.35E-03	2.80E-03	6.99E-04	6.72E-04	6.99E-04
Confidence interval	3.62E-03	1.93E-03	5.84E-03	6.95E-03	1.74E-03	1.67E-03	1.74E-03
WAXFIX 50 wt%							
Replicate 1	1.04E-02	1.85E-02	3.93E-02	1.55E-02	1.28E-02	9.07E-03	7.39E-03
Replicate 2	9.74E-03	1.11E-02	1.58E-02	1.55E-02	1.04E-02	1.41E-02	1.21E-02
Replicate 3	8.74E-03	1.14E-02	2.15E-02	1.88E-02	1.41E-02	1.18E-02	1.01E-02
Mean	9.63E-03	1.37E-02	2.55E-02	1.66E-02	1.24E-02	1.16E-02	9.86E-03
Standard deviation	8.46E-04	4.17E-03	1.23E-02	1.94E-03	1.87E-03	2.52E-03	2.36E-03
Confidence interval	2.10E-03	1.04E-02	3.05E-02	4.82E-03	4.65E-03	6.27E-03	5.86E-03
Polysiloxane 0 wt%							
Replicate 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Replicate 2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Replicate 3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mean	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Standard deviation	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Confidence interval	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Polysiloxane 25 wt%							
Replicate 1	6.72E-04	1.38E-03	4.44E-03	5.48E-03	5.61E-03	4.57E-03	5.41E-03
Replicate 2	4.37E-04	1.14E-03	5.07E-03	5.34E-03	5.11E-03	5.98E-03	5.88E-03
Replicate 3	8.06E-04	1.34E-03	4.80E-03	6.08E-03	5.64E-03	5.64E-03	4.87E-03

Table Q-5. (continued).

Sample	2 Hours Leach #1 (pCi/mL)	7 Hours Leach #2 (pCi/mL)	24 Hours Leach #3 (pCi/mL)	48 Hours Leach #4 (pCi/mL)	72 Hours Leach #5 (pCi/mL)	96 Hours Leach #6 (pCi/mL)	120 Hours Leach #7 (pCi/mL)
Mean	6.38E-04	1.29E-03	4.77E-03	5.63E-03	5.45E-03	5.40E-03	5.39E-03
Standard deviation	1.87E-04	1.27E-04	3.21E-04	3.94E-04	3.01E-04	7.37E-04	5.04E-04
Confidence interval	4.65E-04	3.16E-04	7.96E-04	9.78E-04	7.48E-04	1.83E-03	1.25E-03
Polysiloxane 50 wt%							
Replicate 1	1.31E-03	3.36E-03	1.24E-02	1.68E-02	1.21E-02	1.21E-02	1.78E-02
Replicate 2	1.44E-02	7.06E-03	2.42E-02	3.12E-02	2.62E-02	2.08E-02	2.39E-02
Replicate 3	8.40E-04	2.96E-03	1.31E-02	2.32E-02	1.85E-02	1.78E-02	1.61E-02
Mean	5.53E-03	4.46E-03	1.66E-02	2.37E-02	1.89E-02	1.69E-02	1.93E-02
Standard deviation	7.72E-03	2.26E-03	6.60E-03	7.24E-03	7.07E-03	4.44E-03	4.06E-03
Confidence interval	1.92E-02	5.61E-03	1.64E-02	1.80E-02	1.76E-02	1.10E-02	1.01E-02

Green shading indicates measurements that were below detection. The detection limit was used in these cases. If two-thirds or more of replicates were nondetect, then the mean was treated as nondetect.

Table Q-6. American Nuclear Society leach index results for uranium (must be greater than 6).

Grout	Waste Loading (wt%)	Uranium Leach Index	Confidence Interval C _{99,9}	Minimum Leach Index	Maximum Leach Index	Uranium Leached in 25-wt% Sample (%)
Saltstone ^a	25	16.3	0.8	15.5	17.1	0.002
Saltstone ^a	50	15.8	1.9	13.9	17.7	0.01
WAXFIX	25	8.9	0.4	8.5	9.3	7.7
WAXFIX	50	8.6	0.4	8.2	9.0	10.8
Polysiloxane	25	9.3	1.2	8.1	10.5	5.7
Polysiloxane	50	8.9	1.3	7.6	10.2	9.7

a. Values for Saltstone are suspect due to bleed water.

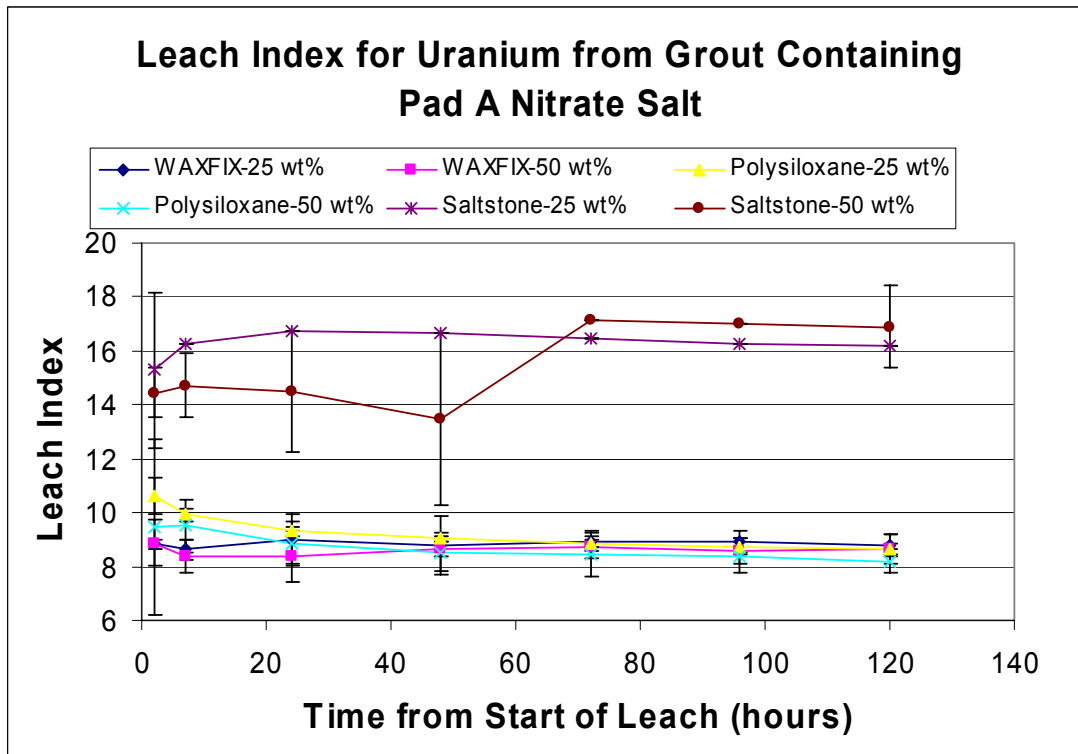


Figure Q-12. American Nuclear Society 16.1 leach indices for uranium in grouts with several weight-percent loadings of Pad A nitrate salts.

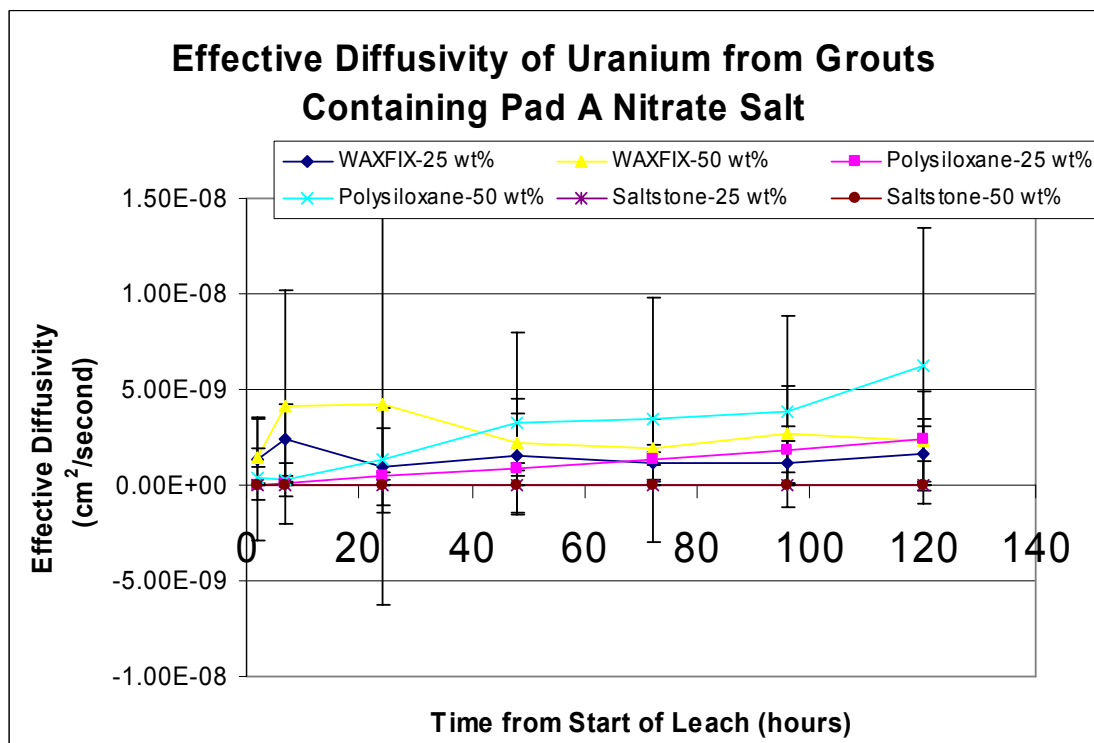


Figure Q-13. Diffusivity of uranium from grouts containing Pad A nitrate salts.

Since the Saltstone samples showed so little uranium leaching, the bleed water was again suspected. In the bleed water, a total of 0.12 mg of uranium was found for the 25-wt% sample and 0.1 mg for the 50-wt% sample. These represent 2.3% and 1.4% of the total uranium in the 25- and 50-wt% samples, respectively. Thus, it is thought that the majority of uranium is retained in the grout waste form.

The measured concentrations of nitrate in the leachate as a function of time are shown in Figure Q-14. Individual values are shown in Table Q-7. The simulated groundwater and grout controls (0 wt% waste) all show nearly the same nonzero concentrations; values range from 5.6 to 8.8 (except for one reading of 78.1, which is considered an outlier). The mean concentration of the simulated groundwater was 6 mg/L; this value was treated as an offset and was accounted for in the subsequent calculations of cumulative weight percent leached and leach index. The Saltstone-25, WAXFIX-25, WAXFIX-50, Polysiloxane-25, and Polysiloxane-50 show similar nitrate leach results over time (see Figure Q-15). Individual values are listed in Table Q-8. Saltstone-50 shows an extremely high leach rate at first and then slows to almost nothing at later times. This suggests that most of the nitrate leaches immediately, and none is left to leach in the later intervals. This again indicates that the Saltstone-50 formulation is unstable as a waste form. It is thought that the very high nitrate concentration in this formulation may be the problem. The overall leach index values for nitrate are presented in Table Q-9. Except for 25 wt% loading of Saltstone, no significant difference was observed between the grouts and waste loadings.

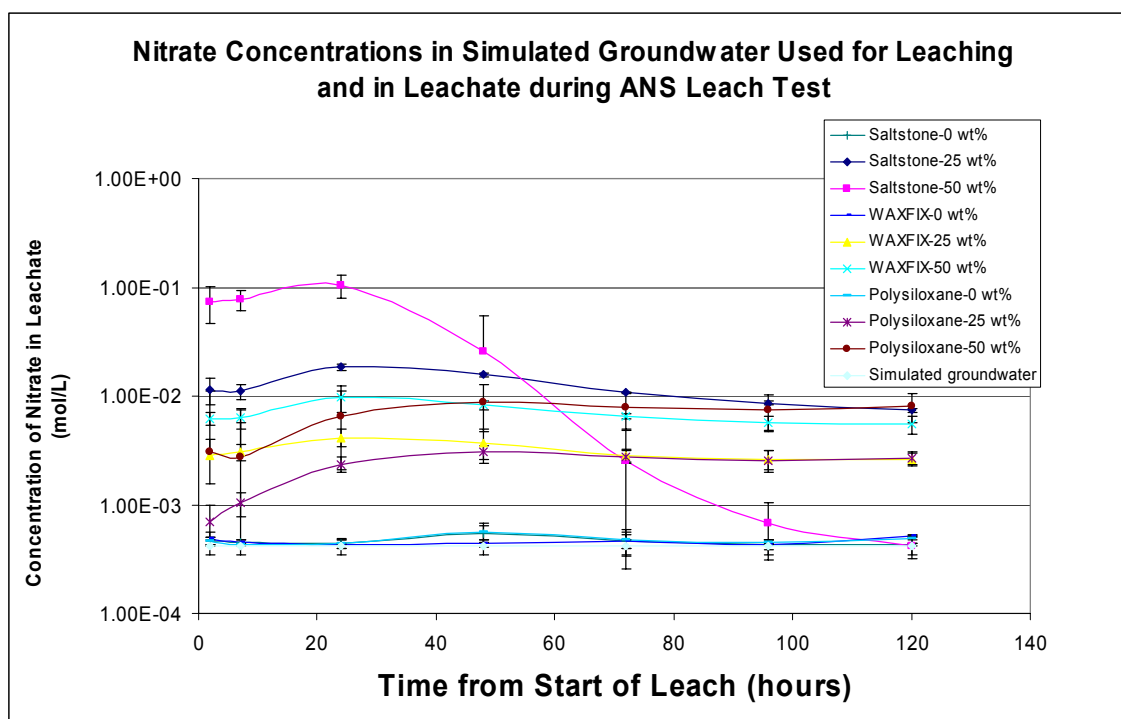


Figure Q-14. Pad A leachate nitrate results.

Table Q-7. Pad A leachate nitrate results.

Sample	2 Hours Leach #1 Nitrate (mol/L)	7 Hours Leach #2 Nitrate (mol/L)	24 Hours Leach #3 Nitrate (mol/L)	48 Hours Leach #4 Nitrate (mol/L)	72 Hours Leach #5 Nitrate (mol/L)	96 Hours Leach #6 Nitrate (mol/L)	120 Hours Leach #7 Nitrate (mol/L)
Saltstone 0 wt%							
Replicate 1	4.85E-04	5.39E-03	4.57E-04	5.34E-04	4.45E-04	4.52E-04	4.22E-04
Replicate 2	4.63E-04	4.54E-04	4.30E-04	5.84E-04	4.28E-04	4.15E-04	4.21E-04
Replicate 3	4.54E-04	4.41E-04	4.29E-04	5.03E-04	5.22E-04	4.22E-04	4.29E-04
Mean	4.67E-04	4.47E-04	4.39E-04	5.41E-04	4.65E-04	4.30E-04	4.24E-04
Standard deviation	1.60E-05	2.85E-03	1.58E-05	4.10E-05	5.02E-05	1.99E-05	4.54E-06
Confidence interval	3.99E-05	7.09E-03	3.91E-05	1.02E-04	1.25E-04	4.95E-05	1.13E-05
Saltstone 25 wt%							
Replicate 1	1.12E-02	1.09E-02	1.80E-02	1.56E-02	1.08E-02	8.70E-03	7.49E-03
Replicate 2	1.03E-02	1.04E-02	1.84E-02	1.54E-02	1.07E-02	8.41E-03	7.31E-03
Replicate 3	1.27E-02	1.18E-02	1.91E-02	1.58E-02	1.08E-02	8.52E-03	7.31E-03
Mean	1.14E-02	1.10E-02	1.85E-02	1.56E-02	1.08E-02	8.54E-03	7.37E-03
Standard deviation	1.23E-03	7.36E-04	5.32E-04	2.34E-04	6.18E-05	1.43E-04	9.94E-05
Confidence interval	3.06E-03	1.83E-03	1.32E-03	5.80E-04	1.54E-04	3.56E-04	2.47E-04
Saltstone 50 wt%							
Replicate 1	8.62E-02	8.34E-02	9.85E-02	1.22E-02	1.48E-03	5.10E-04	3.72E-04
Replicate 2	6.83E-02	7.09E-02	9.82E-02	3.33E-02	3.15E-03	7.88E-04	4.39E-04
Replicate 3	6.65E-02	7.68E-02	1.16E-01	3.09E-02	2.95E-03	7.45E-04	4.44E-04
Mean	7.37E-02	7.70E-02	1.04E-01	2.55E-02	2.53E-03	6.81E-04	4.18E-04
Standard deviation	1.09E-02	6.27E-03	9.94E-03	1.15E-02	9.15E-04	1.50E-04	4.02E-05
Confidence interval	2.71E-02	1.56E-02	2.47E-02	2.86E-02	2.27E-03	3.72E-04	9.98E-05
WAXFIX 0 wt%							
Replicate 1	4.69E-04	4.44E-04	4.38E-04	4.32E-04	4.66E-04	4.30E-04	5.12E-04
Replicate 2	5.15E-04	4.59E-04	4.32E-04	4.32E-04	4.32E-04	4.38E-04	5.08E-04
Replicate 3	4.74E-04	4.57E-04	4.32E-04	4.57E-04	4.88E-04	4.30E-04	5.15E-04
Mean	4.95E-04	4.53E-04	4.34E-04	4.40E-04	4.62E-04	4.33E-04	5.12E-04
Standard deviation	2.52E-05	8.25E-06	3.34E-06	1.45E-05	2.85E-05	4.17E-06	3.40E-06
Confidence interval	6.26E-05	2.05E-05	8.29E-06	3.60E-05	7.08E-05	1.03E-05	8.45E-06
WAXFIX 25 wt%							
Replicate 1	3.29E-03	3.05E-03	4.49E-03	4.07E-03	2.98E-03	2.66E-03	2.71E-03
Replicate 2	2.77E-03	3.27E-03	3.89E-03	3.08E-03	2.70E-03	2.41E-03	2.47E-03
Replicate 3	2.30E-03	2.84E-03	4.05E-03	3.80E-03	2.86E-03	2.83E-03	2.70E-03
Mean	2.79E-03	3.05E-03	4.14E-03	3.65E-03	2.85E-03	2.63E-03	2.63E-03
Standard deviation	4.97E-04	2.18E-04	3.10E-04	5.13E-04	1.42E-04	2.10E-04	1.32E-04
Confidence interval	1.23E-03	5.41E-04	7.69E-04	1.27E-03	3.53E-04	5.22E-04	3.27E-04

Table Q-7. (continued).

Sample	2 Hours Leach #1 Nitrate (mol/L)	7 Hours Leach #2 Nitrate (mol/L)	24 Hours Leach #3 Nitrate (mol/L)	48 Hours Leach #4 Nitrate (mol/L)	72 Hours Leach #5 Nitrate (mol/L)	96 Hours Leach #6 Nitrate (mol/L)	120 Hours Leach #7 Nitrate (mol/L)
WAXFIX 50 wt%							
Replicate 1	6.01E-03	6.94E-03	1.08E-02	8.19E-03	6.58E-03	5.35E-03	5.07E-03
Replicate 2	6.62E-03	5.87E-03	8.70E-03	8.03E-03	6.38E-03	5.99E-03	5.89E-03
Replicate 3	5.99E-03	6.22E-03	9.67E-03	8.61E-03	6.62E-03	5.66E-03	5.63E-03
Mean	6.21E-03	6.34E-03	9.73E-03	8.28E-03	6.53E-03	5.67E-03	5.53E-03
Standard deviation	3.57E-04	5.42E-04	1.07E-03	3.00E-04	1.27E-04	3.20E-04	4.18E-04
Confidence interval	8.88E-04	1.35E-03	2.65E-03	7.44E-04	3.14E-04	7.96E-04	1.04E-03
Polysiloxane 0 wt%							
Replicate 1	4.74E-04	4.18E-04	4.63E-04	5.24E-04	4.52E-04	4.46E-04	4.80E-04
Replicate 2	4.44E-04	4.29E-04	4.32E-04	5.47E-04	4.63E-04	4.54E-04	5.03E-04
Replicate 3	4.59E-04	4.29E-04	4.33E-04	6.10E-04	5.17E-04	4.65E-04	4.71E-04
Mean	4.59E-04	4.29E-04	4.43E-04	5.60E-04	4.77E-04	4.55E-04	4.85E-04
Standard deviation	1.52E-05	6.50E-06	1.76E-05	4.48E-05	3.45E-05	9.13E-06	1.66E-05
Confidence interval	3.79E-05	1.62E-05	4.38E-05	1.11E-04	8.57E-05	2.27E-05	4.13E-05
Polysiloxane 25 wt%							
Replicate 1	6.97E-04	1.02E-03	2.32E-03	2.85E-03	2.59E-03	2.33E-03	2.55E-03
Replicate 2	5.88E-04	9.43E-04	2.23E-03	3.08E-03	2.78E-03	2.52E-03	2.65E-03
Replicate 3	8.15E-04	1.14E-03	2.52E-03	3.22E-03	2.89E-03	2.78E-03	2.84E-03
Mean	7.00E-04	1.04E-03	2.36E-03	3.05E-03	2.75E-03	2.54E-03	2.68E-03
Standard deviation	1.13E-04	1.01E-04	1.51E-04	1.83E-04	1.52E-04	2.25E-04	1.45E-04
Confidence interval	2.82E-04	2.52E-04	3.74E-04	4.56E-04	3.77E-04	5.60E-04	3.60E-04
Polysiloxane 50 wt%							
Replicate 1	1.17E-03	2.01E-03	5.23E-03	7.19E-03	6.62E-03	6.28E-03	7.22E-03
Replicate 2	6.84E-03	4.12E-03	8.61E-03	1.04E-02	9.02E-03	8.41E-03	9.14E-03
Replicate 3	1.24E-03	2.20E-03	5.85E-03	8.50E-03	8.06E-03	7.74E-03	8.00E-03
Mean	3.08E-03	2.77E-03	6.56E-03	8.70E-03	7.90E-03	7.48E-03	8.12E-03
Standard deviation	3.26E-03	1.17E-03	1.80E-03	1.62E-03	1.21E-03	1.09E-03	9.66E-04
Confidence interval	8.09E-03	2.90E-03	4.47E-03	4.01E-03	3.00E-03	2.71E-03	2.40E-03

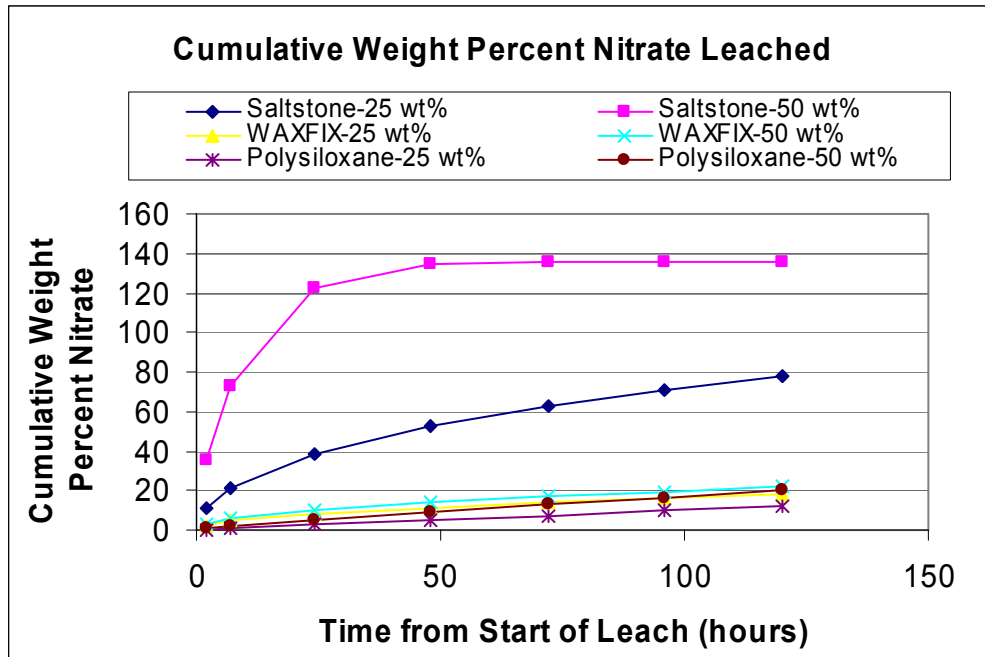


Figure Q-15. Cumulative weight percent of nitrate leached.

Table Q-8. Cumulative weight percent of nitrate leached.

Time (hours)	Saltstone 25 wt% Cumulative Leached (%)	Saltstone 50 wt% Cumulative Leached (%)	WAXFIX 25 wt% Cumulative Leached (%)	WAXFIX 50 wt% Cumulative Leached (%)	Polysiloxane 25 wt% Cumulative Leached (%)	Polysiloxane 50 wt% Cumulative Leached (%)
2	9.7	31.2	2.4	2.6	0.6	1.3
7	19.0	63.8	4.9	5.3	1.5	2.5
24	34.7	107.9	8.5	9.4	3.5	5.3
48	47.9	118.7	11.5	12.9	6.0	8.9
72	57.0	119.7	14.0	15.7	8.4	12.3
96	64.2	120.0	16.2	18.1	10.5	15.5
120	70.5	120.2	18.4	20.4	12.8	18.9

Table Q-9. Calculated leach indices for nitrate.

Grout	Waste Loading (wt%)	Leach Index	99.9% Confidence Interval
Saltstone	25	6.9	0.2
	50	8.0	4.3
WAXFIX	25	8.1	0.2
	50	8.0	0.1
Polysiloxane	25	8.7	1.2
	50	8.2	1.0

In addition to uranium and nitrate, solution pH and ORP were measured in each of the ANS leachates (Tables Q-10 and Q-11). The means of the triplicate pH measurements are presented in Figure Q-16. Individual pH readings are available in Tables Q-12–Q-14. The Saltstone-25, WAXFIX-25, WAXFIX-50, Polysiloxane-25, and Polysiloxane-50 all show a very consistent pH around 8, whereas the Saltstone-50 showed a high change in pH from 10 to 10.5. This change indicated an unstable grout formulation in that more caustic is being produced and not utilized by the hydration reactions. The solution ORP is plotted in Figure Q-17 (individual measurements are shown in Table Q-15) and shows an inverse relation to solution pH. Again, the five grout samples noted above were consistent in ORP grouped around +200 mV, and the Saltstone-50 stood out as a negative ORP. The negative ORP indicates that the leach solution is reduced while the ORP of the other grouts is oxidized. The five grouts exhibit a more linear leach trend over the intervals, thus indicating a steady leach rate. The Saltstone-50 exhibits a curved leach rate, indicating a changing leach rate where more ions are leached in the middle intervals, and then the rate tapers off in the later intervals.

Table Q-10. Pad A oxidation-reduction potential leach results for Polysiloxane.

Sample	2 Hours Leach #1 (ORP)	5 Hours Leach #2 (ORP)	24 Hours Leach #3 (ORP)	48 Hours Leach #4 (ORP)	72 Hours Leach #5 (ORP)	96 Hours Leach #6 (ORP)	120 Hours Leach #7 (ORP)
Polysiloxane 0 wt%							
Replicate 1	220.2	216.5	233.5	236.5	228.6	218.1	203.2
Replicate 2	216.3	210.7	227.9	239.0	208.9	211.1	194.7
Replicate 3	212.0	201.1	231.7	234.2	215.1	213.1	199.2
Mean	216.17	209.43	231.03	236.57	217.53	214.10	199.03
Standard deviation	4.10	7.78	2.86	2.40	10.07	3.61	4.25
Confidence interval	1.02E+01	1.93E+01	7.10E+00	5.96E+00	2.50E+01	8.96E+00	1.06E+01
Polysiloxane 25 wt%							
Replicate 1	221.2	227.7	219.4	197.8	198.9	204.2	196.2
Replicate 2	224.6	226.5	212.6	203.8	200.3	203.1	192.1
Replicate 3	227.3	227.0	207.7	200.5	198.9	200.4	191.1
Mean	224.37	227.07	213.23	200.70	199.37	202.57	193.13
Standard deviation	3.06	0.60	5.88	3.00	0.81	1.96	2.70
Confidence interval	7.59E+00	1.50E+00	1.46E+01	7.47E+00	2.01E+00	4.86E+00	6.71E+00
Polysiloxane 50 wt%							
Replicate 1	282.2	262.6	226.3	210.0	233.2	223.3	154.2
Replicate 2	269.0	248.4	214.2	198.3	223.0	201.3	140.8
Replicate 3	280.6	248.5	213.2	198.4	218.3	161.8	144.1
Mean	277.27	253.17	217.90	202.23	224.83	195.47	146.37
Standard deviation	7.20	8.17	7.29	6.73	7.62	31.16	6.98
Confidence interval	1.79E+01	2.03E+01	1.81E+01	1.67E+01	1.89E+01	7.74E+01	1.73E+01

ORP = oxidation-reduction potential

Table Q-11. Pad A oxidation-reduction potential leach results for WAXFIX.

Sample	2 Hours Leach #1 (ORP)	7 Hours Leach #2 (ORP)	24 Hours Leach #3 (ORP)	48 Hours Leach #4 (ORP)	72 Hours Leach #5 (ORP)	96 Hours Leach #6 (ORP)	120 Hours Leach #7 (ORP)
WAXFIX 0 wt%							
Replicate 1	218.2	222.5	218.9	216.6	204.4	193.1	222.1
Replicate 2	212.2	219.7	221.5	215.3	204.1	189.2	216.8
Replicate 3	212.9	213.2	220.0	216.9	205.3	188.9	213.5
Mean	214.4	218.5	220.1	216.3	204.6	190.4	217.5
Standard deviation	3.3	4.8	1.3	0.8	0.6	2.3	4.3
Confidence interval	8.2	11.9	3.2	2.1	1.6	5.8	10.8
WAXFIX 25 wt%							
Replicate 1	187.9	167.2	148.0	131.2	164.1	217.3	216.5
Replicate 2	190.4	170.2	151.6	141.1	165.9	217.8	209.0
Replicate 3	189.2	165.1	134.7	146.7	166.9	212.0	207.4
Mean	189.2	167.5	144.8	139.7	165.6	215.7	211.0
Standard deviation	1.2	2.6	8.9	7.8	1.4	3.2	4.9
Confidence interval	3.1	6.4	22.1	19.5	3.5	8.0	12.1
WAXFIX 50 wt%							
Replicate 1	233.2	210.5	187.8	191.8	191.6	190.5	190.5
Replicate 2	221.1	206.4	193.3	190.4	189.4	184.7	183.6
Replicate 3	215.2	202.5	191.3	187.1	185.5	186.5	182.1
Mean	223.2	206.5	190.8	189.8	188.8	187.2	185.4
Standard deviation	9.2	4.0	2.8	2.4	3.1	3.0	4.5
Confidence interval	22.8	9.9	6.9	6.0	7.7	7.4	11.1
ORP = oxidation-reduction potential							

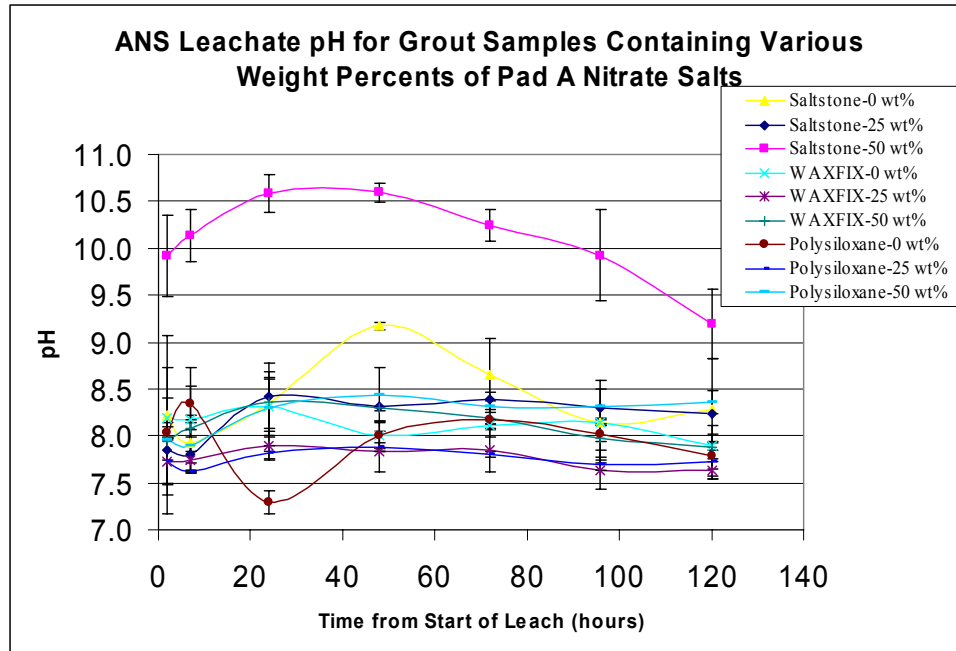


Figure Q-16. Pad A leachate pH results.

Table Q-12. Pad A pH leach results for Polysiloxane.

Sample	2 Hours Leach #1 (pH)	7 Hours Leach #2 (pH)	24 Hours Leach #3 (pH)	48 Hours Leach #4 (pH)	72 Hours Leach #5 (pH)	96 Hours Leach #6 (pH)	120 Hours Leach #7 (pH)
Polysiloxane 0 wt%							
Replicate 1	8.06	8.26	7.24	8.06	8.10	8.02	7.88
Replicate 2	8.04	8.33	7.31	7.93	8.18	7.99	7.70
Replicate 3	8.01	8.42	7.33	8.00	8.26	8.06	7.80
Mean	8.04	8.34	7.29	8.00	8.18	8.02	7.79
Standard deviation	0.03	0.08	0.05	0.07	0.08	0.04	0.09
Confidence interval	0.06	0.20	0.12	0.16	0.20	0.09	0.22
Polysiloxane 25 wt%							
Replicate 1	7.84	7.62	7.79	7.86	7.82	7.71	7.80
Replicate 2	7.70	7.61	7.82	7.89	7.79	7.67	7.75
Replicate 3	7.66	7.61	7.85	7.89	7.80	7.72	7.65
Mean	7.73	7.61	7.82	7.88	7.80	7.70	7.73
Standard deviation	0.09	0.01	0.03	0.02	0.02	0.03	0.08
Confidence interval	0.23	0.01	0.07	0.04	0.04	0.07	0.19
Polysiloxane 50 wt%							
Replicate 1	7.73	7.88	8.18	8.31	8.25	8.22	8.33
Replicate 2	8.31	7.97	8.42	8.53	8.36	8.34	8.41
Replicate 3	7.81	7.83	8.31	8.48	8.35	8.36	8.32
Mean	7.95	7.89	8.30	8.44	8.32	8.31	8.35
Standard deviation	0.31	0.07	0.12	0.12	0.06	0.08	0.05
Confidence interval	0.78	0.18	0.30	0.29	0.15	0.19	0.12

Table Q-13. Pad A pH leach results for WAXFIX.

Sample	2 Hours Leach #1 (pH)	7 Hours Leach #2 (pH)	24 Hours Leach #3 (pH)	48 Hours Leach #4 (pH)	72 Hours Leach #5 (pH)	96 Hours Leach #6 (pH)	120 Hours Leach #7 (pH)
WAXFIX 0 wt%							
Replicate 1	8.28	7.94	8.52	8.05	8.11	8.16	7.92
Replicate 2	8.19	8.39	8.25	8.01	8.12	8.14	7.90
Replicate 3	8.11	8.19	8.15	7.94	8.10	8.15	7.88
Mean	8.19	8.17	8.31	8.00	8.11	8.15	7.90
Standard deviation	0.09	0.23	0.19	0.06	0.01	0.01	0.02
Confidence interval	0.21	0.56	0.48	0.14	0.02	0.02	0.05
WAXFIX 25 wt%							
Replicate 1	7.81	7.77	7.97	7.93	7.95	7.59	7.66
Replicate 2	7.73	7.75	7.87	7.77	7.79	7.59	7.59
Replicate 3	7.62	7.69	7.87	7.79	7.80	7.74	7.64
Mean	7.72	7.74	7.90	7.83	7.85	7.64	7.63
Standard deviation	0.10	0.04	0.06	0.09	0.09	0.09	0.04
Confidence interval	0.24	0.10	0.14	0.22	0.22	0.22	0.09
WAXFIX 50 wt%							
Replicate 1	7.85	8.12	8.47	8.28	8.16	7.88	7.77
Replicate 2	8.01	8.05	8.26	8.29	8.20	8.06	7.93
Replicate 3	7.95	8.07	8.33	8.3	8.21	7.96	7.93
Mean	7.94	8.08	8.35	8.29	8.19	7.97	7.88
Standard deviation	0.08	0.04	0.11	0.01	0.03	0.09	0.09
Confidence interval	0.20	0.09	0.27	0.02	0.07	0.22	0.23

Table Q-14. Pad A pH leach results for Saltstone.

Sample	2 Hours Leach #1 (pH)	7 Hours Leach #2 (pH)	24 Hours Leach #3 (pH)	48 Hours Leach #4 (pH)	72 Hours Leach #5 (pH)	96 Hours Leach #6 (pH)	120 Hours Leach #7 (pH)
Saltstone 0 wt%							
Replicate 1	7.90	8.06	8.42	9.19	8.69	8.07	8.04
Replicate 2	8.18	7.88	8.42	9.17	8.79	8.02	8.40
Replicate 3	8.58	7.83	8.18	9.16	8.49	8.35	8.42
Mean	8.22	7.92	8.34	9.17	8.66	8.15	8.29
Standard deviation	0.34	0.12	0.14	0.02	0.15	0.18	0.21
Confidence interval	0.85	0.30	0.34	0.04	0.38	0.44	0.53
Saltstone 25 wt%							
Replicate 1	7.93	7.77	8.33	8.32	8.29	8.27	8.22
Replicate 2	7.78	7.83	8.46	8.33	8.47	8.33	8.23
Replicate 3	7.84	7.81	8.45	8.31	8.42	8.30	8.25
Mean	7.85	7.80	8.41	8.32	8.39	8.30	8.23
Standard deviation	0.08	0.03	0.07	0.01	0.09	0.03	0.02
Confidence interval	0.19	0.08	0.18	0.02	0.23	0.07	0.04

Table Q-14. (continued).

Sample	2 Hours Leach #1 (pH)	7 Hours Leach #2 (pH)	24 Hours Leach #3 (pH)	48 Hours Leach #4 (pH)	72 Hours Leach #5 (pH)	96 Hours Leach #6 (pH)	120 Hours Leach #7 (pH)
Saltstone 50 wt%							
Replicate 1	10.09	10.26	10.68	10.62	10.17	9.7	9.05
Replicate 2	9.92	10.10	10.54	10.55	10.31	10.06	9.18
Replicate 3	9.74	10.05	10.54	10.62	10.24	10.01	9.35
Mean	9.92	10.14	10.59	10.60	10.24	9.92	9.19
Standard deviation	0.18	0.11	0.08	0.04	0.07	0.20	0.15
Confidence interval	0.43	0.27	0.20	0.10	0.17	0.48	0.37

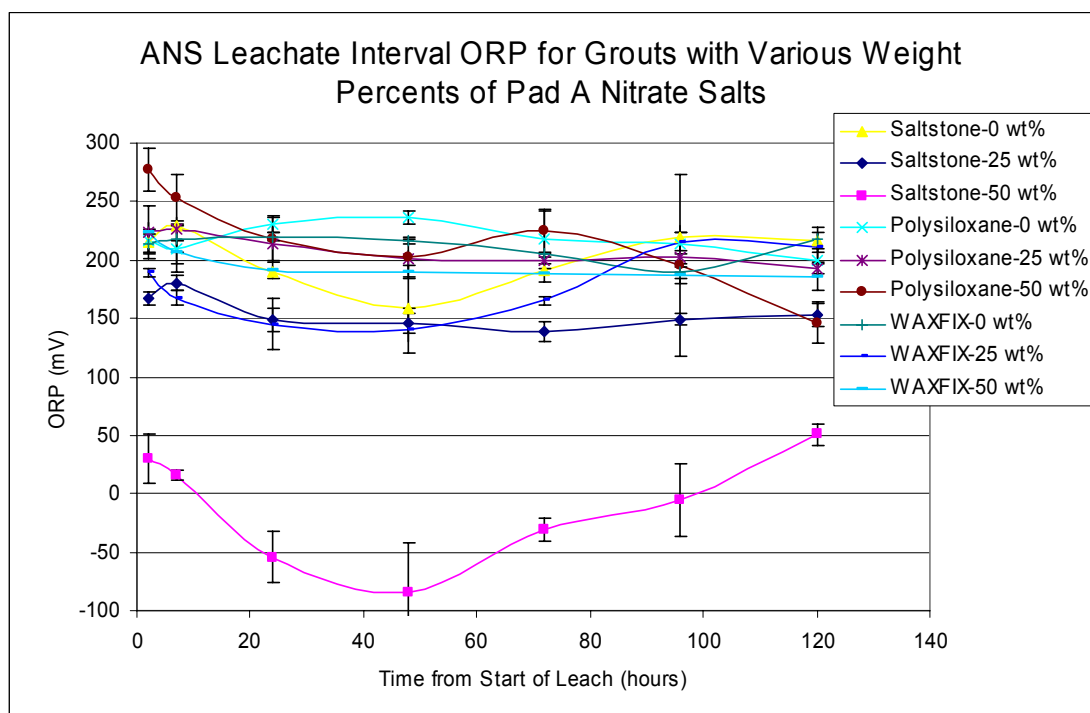


Figure Q-17. Pad A oxidation-reduction potential leachate results.

Table Q-15. Pad A oxidation-reduction potential leach results for Saltstone.

Sample	2 Hours Leach #1 (ORP)	7 Hours Leach #2 (ORP)	24 Hours Leach #3 (ORP)	48 Hours Leach #4 (ORP)	72 Hours Leach #5 (ORP)	96 Hours Leach #6 (ORP)	120 Hours Leach #7 (ORP)
Saltstone 0 wt%							
Replicate 1	217.1	*231.3	187.4	147.2	192.2	221.0	218.0
Replicate 2	216.0	226.9	190.6	169.5	190.3	222.0	217.9
Replicate 3	210.4	231.0	190.5	158.8	191.7	214.1	213.4
Mean	214.5	229.0	189.5	158.5	191.4	219.0	216.4
Standard deviation	3.6	2.9	1.8	11.2	1.0	4.3	2.6
Confidence interval	8.9	7.2	4.5	27.7	2.4	10.7	6.5

Table Q-15. (continued).

Sample	2 Hours Leach #1 (ORP)	7 Hours Leach #2 (ORP)	24 Hours Leach #3 (ORP)	48 Hours Leach #4 (ORP)	72 Hours Leach #5 (ORP)	96 Hours Leach #6 (ORP)	120 Hours Leach #7 (ORP)
Saltstone 25 wt%							
Replicate 1	169.8	182.9	153.6	149.8	141.3	147.7	157.7
Replicate 2	166.9	178.5	148.0	145.9	135.2	149.3	151.8
Replicate 3	164.7	178.4	146.0	143.1	140.8	151.2	150.4
Mean	167.1	179.9	149.2	146.3	139.1	149.4	153.3
Standard deviation	2.5	2.6	3.9	3.4	3.4	1.8	3.9
Confidence interval	6.4	6.4	9.8	8.4	8.4	4.4	9.6
Saltstone 50 wt%							
Replicate 1	23.0	13.9	-46.5	-64.5	-35.0	8.4	54.5
Replicate 2	28.9	16.4	-52.1	-92.0	-31.7	-15.7	50.6
Replicate 3	39.9	17.1	-63.8	-94.8	-27.0	-8.8	47.4
Mean	30.6	15.8	-54.1	-83.8	-31.2	-5.4	50.8
Standard deviation	8.6	1.7	8.8	16.7	4.0	12.4	3.6
Confidence interval	21.3	4.2	21.9	41.6	10.0	30.8	8.8

ORP = oxidation-reduction potential

Q-6. EXAMPLE CALCULATIONS FOR PAD A LEACH INDEX

The following is an example of how leach indices were calculated in this appendix.

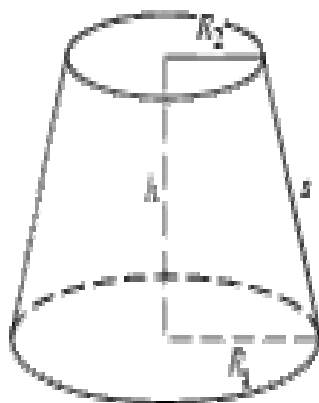


Figure Q-18. Diagram of specimen.

Specimen—conical frustum (see Figure Q-18)

Top diameter = 1.80 cm

Bottom diameter = 1.90 cm

$R_2 = 0.90$ cm

$R_1 = 0.95$ cm

$h = 3.10$ cm

For these sample calculations, the WAXFIX 50-wt% specimen is used:

Mold tare = 257.4 g

Grout and mold = 288 g (made three frustum specimens)

Waste loading = 50%

Pad A waste data:

Analysis = 0.327 g Pad A in 100 mL water

Results = 385 ppb U-238 in solution

= 5.17 ppb U-235 in solution

Sample volume:

$$V = 1/3 \pi h (R_1^2 + R_1 R_2 + R_2^2)$$

$$V = 1/3 \pi (3.1)(0.95^2 + (0.95)(0.90) + 0.90^2)$$

$$V = 8.33 \text{ cm}^3$$

Sample surface area:

A = side + top + bottom areas

$$A = \pi (R_1 + R_2)((R_1 - R_2)^2 + h^2)^{1/2} + \pi R_1^2 + \pi R_2^2$$

$$A = \pi (0.95 + 0.9)((0.95 - 0.9)^2 + 3.1^2)^{1/2} + \pi 0.95^2 + \pi 0.9^2$$

$$A = 1.85 \pi (3.10) + 0.903 \pi + 0.81 \pi$$

Specimen grout:

$$\text{Total three-specimen mass} = 288.0 \text{ g} - 257.4 \text{ g} = 30.6 \text{ g}$$

$$\text{Each specimen} = 30.6 \text{ g} / 3 = 10.2 \text{ g}$$

$$\text{Specimen density} = 30.6 \text{ g} / 8.33 \text{ cm}^3 / 3 = 1.22 \text{ g} / \text{cm}^3$$

At 50% loading:

$$\text{Pad A in specimen} = (10.2 \text{ g})(50\%) = 5.1 \text{ g}$$

Uranium in Pad A:

U-238 =	$\frac{385 \text{ g U}}{1\text{E}+09 \text{ g soln}}$	$\frac{100 \text{ g soln}}{0.327 \text{ g Pad A}}$	$\frac{3.36\text{E}-7 \text{ Ci}}{\text{g U}}$	$\frac{1\text{E}+12 \text{ pCi}}{\text{Ci}}$	= 39.6 pCi
U-235 =	$\frac{5.17 \text{ g U}}{1\text{E}+09 \text{ g soln}}$	$\frac{100 \text{ g soln}}{0.327 \text{ g Pad A}}$	$\frac{2.16\text{E}-6 \text{ Ci}}{\text{g U}}$	$\frac{1\text{E}+12 \text{ pCi}}{\text{Ci}}$	= 3.4 pCi
Total U =	39.6 + 3.4 = 43.0 pCi/g Pad A				

Uranium in Pad A WAXFIX specimen:

$$U = \frac{43 \text{ pCi}}{\text{g Pad A}} \frac{0.5 \text{ g Pad A}}{1 \text{ g specimen}} \frac{10.2 \text{ g specimen}}{1 \text{ g specimen}} = 219.3 \text{ pCi U}$$

ANS leach:

Used 234 mL water (10 times surface area) for each leachant at 2-, 5-, 17-, 24-, 24-, 24-, and 24-hour intervals (seven total per specimen).

Table Q-16. Leach results—uranium in parts per billion.

Specimen	2 Hours	5 Hours	17 Hours	24 Hours	24 Hours	24 Hours	24 Hours
Replicate 1	31.0	55.0	117.0	46.0	38.0	27.0	22.0
Replicate 2	29.0	33.0	47.0	46.0	31.0	42.0	36.0
Replicate 3	26.0	34.0	64.0	56.0	42.0	35.0	30.0
Mean	28.7	40.7	76.0	49.3	37.0	34.7	29.3
Standard deviation	2.5	12.4	36.5	5.8	5.6	7.5	7.0
pCi/g solution	9.6E-03	1.4E-02	2.6E-02	1.7E-02	1.2E-02	1.2E-02	9.9E-03
pCi	2.2	3.3	6.1	4.0	2.8	2.8	2.3

Sample calculations for Table Q-16:

Mean 2 hours = $(31 + 29 + 26) / 3 = 28.7$ ppb

Standard deviation = $((n \sum x^2 - (\sum x)^2) / n(n-1))^{1/2}$

Standard deviation = $((3)(2478) - 86^2) / (3)(2))^{1/2} = 2.52$

$$\text{pCi/g} = \frac{28.7 \text{ g U}}{1\text{E}+9 \text{ g soln}} \mid \frac{3.36\text{E}-7 \text{ Ci}}{\text{g U}} \mid \frac{1\text{E}+12 \text{ pCi}}{\text{Ci}} = 9.6\text{E}-3 \text{ pCi / g soln}$$
 (assumes all U to be U-238)

pCi leached = $9.6\text{E}-3 \text{ pCi} \mid 234 \text{ g soln} = 2.2 \text{ pCi U in 2-hour leachant/g soln}$

Table Q-17. American Nuclear Society leach interval time.

Interval	Hours	Seconds	Cumulative (seconds)	Time (mean seconds)
1	2	7,200	7,200	1,800.0
2	5	18,000	25,200	14,835.0
3	17	61,200	86,400	51,230.7
4	24	86,400	172,800	125,894.0
5	24	86,400	259,200	213,818.0
6	24	86,400	345,600	300,849.0
7	24	86,400	432,000	387,596.3

From ANS, mean time (T) is defined as in Equation (Q-1):

$$T_n = [1/2 (t_n^{1/2} + t_{n-1}^{1/2})]^2 \quad (\text{Q-1})$$

where:

t_n cumulative leaching time for interval (from Table Q-17)

T_1 $[1/2 (7,200^{1/2} + 0^{1/2})]^2 = 1,800.0$ seconds

T_2 $[1/2 (25,200^{1/2} + 7,200^{1/2})]^2 = 14,835.0$ seconds

$$\begin{aligned}
T_3 &= [1/2 (86,400^{1/2} + 25,200^{1/2})]^2 = 51,230.7 \text{ seconds} \\
T_4 &= [1/2 (172,800^{1/2} + 86,400^{1/2})]^2 = 125,894.0 \text{ seconds} \\
T_5 &= [1/2 (259,200^{1/2} + 172,800^{1/2})]^2 = 213,818.0 \text{ seconds} \\
T_6 &= [1/2 (345,600^{1/2} + 259,200^{1/2})]^2 = 300,849.2 \text{ seconds} \\
T_7 &= [1/2 (432,000^{1/2} + 345,600^{1/2})]^2 = 387,596.3 \text{ seconds.}
\end{aligned}$$

ANS diffusivity is shown in Equation (Q-2):

$$D_n = \pi [a_n / A_0 / (\Delta t)_n]^2 [V / S]^2 T_n \quad (Q-2)$$

where:

$$\begin{aligned}
a_n &= \text{pCi leached} \\
A_0 &= \text{original pCi in sample} = 219.3 \text{ pCi of uranium} \\
(\Delta t)_n &= \text{leach duration} \\
V &= \text{specimen volume} = 8.33 \text{ cm}^3 \\
S &= \text{specimen surface area} = 23.40 \text{ cm}^2 \\
T_n &= \text{mean time leach interval} \\
D_1 &= \pi [2.2 / 219.3 / 7,200]^2 [8.33 / 23.40]^2 (1,800.0) = 1.39\text{E}-9 \\
D_2 &= \pi [3.3 / 219.3 / 18,000]^2 [8.33 / 23.40]^2 (14,835.0) = 4.13\text{E}-9 \\
D_3 &= \pi [6.1 / 219.3 / 61,200]^2 [8.33 / 23.40]^2 (51,230.7) = 4.21\text{E}-9 \\
D_4 &= \pi [4.0 / 219.3 / 86,400]^2 [8.33 / 23.40]^2 (125,894.0) = 2.23\text{E}-9 \\
D_5 &= \pi [2.8 / 219.3 / 86,400]^2 [8.33 / 23.40]^2 (213,818.0) = 1.86\text{E}-9 \\
D_6 &= \pi [2.8 / 219.3 / 86,400]^2 [8.33 / 23.40]^2 (300,849.0) = 2.62\text{E}-9 \\
D_7 &= \pi [2.3 / 219.3 / 86,400]^2 [8.33 / 23.40]^2 (387,596.3) = 2.27\text{E}-9.
\end{aligned}$$

ANS leach index is shown in Equation (Q-3):

$$\text{Leach index} = 1/n \sum [\log (\beta / D_n)]_n \quad (Q-3)$$

$$\text{Interval index} = \log (\beta / D_n)$$

where:

$$\begin{aligned}
\beta &= \text{constant} = 1.0 \text{ cm}^2/\text{s} \\
I_1 &= \log (1 / 1.39\text{E}-09) = 8.86 \approx 8.8 \\
I_2 &= \log (1 / 4.13\text{E}-09) = 8.38 \approx 8.4 \\
I_3 &= \log (1 / 4.21\text{E}-09) = 8.38 \approx 8.4 \\
I_4 &= \log (1 / 2.23\text{E}-09) = 8.65 \approx 8.6 \\
I_5 &= \log (1 / 1.86\text{E}-09) = 8.73 \approx 8.7 \\
I_6 &= \log (1 / 2.62\text{E}-09) = 8.58 \approx 8.6
\end{aligned}$$

$$I_7 = \log (1 / 2.27\text{E-}09) = 8.64 \approx 8.6$$

$$L_i = 8.6.$$

Q-7. REFERENCES

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Appendix R

Compressive-Strength Tests—Part 2

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Appendix R

Compressive-Strength Tests—Part 2

For full-scale in situ grouting at the Subsurface Disposal Area, grouted waste columns must provide a stable foundation for material placed on it, including caps and cover material. Subsidence of soil into subsurface voids during wet conditions is undesirable because soil subsidence causes ponding of surface water, which may lead to an increase in permeable pathways to the waste. Selecting a grout with an adequate compressive strength for jet grouting is expected to reduce the potential for subsidence. For this bench study, a compressive strength of 250 psig is the criterion for acceptability. Samples of neat grout and grout mixed with soil were tested for unconfined compressive strength.

Commercially available Portland cement grout, both neat and mixed with ASTM International-certified blast furnace slag, was compared to GMENT-12 when mixed with soil at a loading of 30 and 50 wt% soil by weight for compressive strength. Table R-1 provides a list of grouts being tested and loadings at which the tests were conducted. This comparison gives confidence in bench-derived data to evaluate future grout types for application of in situ grouting of buried waste. Test results and observations were used to determine the waste-loading tolerance for grout materials.

Table R-1. Summary of compressive-strength testing of cold surrogates for grout with soil from the Idaho National Laboratory Site.

Test Method	Measurement/ Analytical Method	Grouts	Soil in Grout (wt%)	Replicates	Total Samples
ASTM C39, ASTM D695	Unconfined compressive strength (pounds per square inch)	GMEN-12 Portland Type II Portland Type II and blast furnace slag (50:50 mixture by weight)	0 30 50	5	45

R-1. TEST OBJECTIVES AND RATIONALE

The main goals for in situ grouting are physical stabilization of waste and immobilization of contaminants of concern. The injected grout mixture will stabilize buried waste by filling voids in the waste and associated soils, preventing site subsidence and ponding of surface water.

Compressive strength was used as an objective standard for defining cohesive (i.e., stand-alone) contiguous columns and determining the maximum waste loading for a grout. Previous work with grout and waste mixtures has shown that unconfined compressive strength is both a good indicator for cohesive contiguous columns and a good predictor for maximum waste loading for a grout.

R-2. EXPERIMENTAL DESIGN AND PROCEDURES

Soil from the Idaho National Laboratory Site was used in this test to simulate waste in nontransuranic pits and trenches and soil vault rows.

R-3. EQUIPMENT AND MATERIALS

Neat grout samples and mixtures of grout and soil from the Idaho National Laboratory Site (sieved to 10 mesh) were mixed at 30 and 50 wt% soil and allowed to cure for 30 days at a constant humidity

(98–99%). Samples were prepared using 5-cm (2-in.)-diameter by 10-cm (4-in.)-tall plastic molds (see Figure R-1). Compressive strength was tested using an Instron 4505 screw-driven load frame with a 22.48-kip load cell (see Figure R-2). Data were collected electronically using LabVIEW as the data acquisition platform.



Figure R-1. Grout samples prepared for compressive-strength measurements.

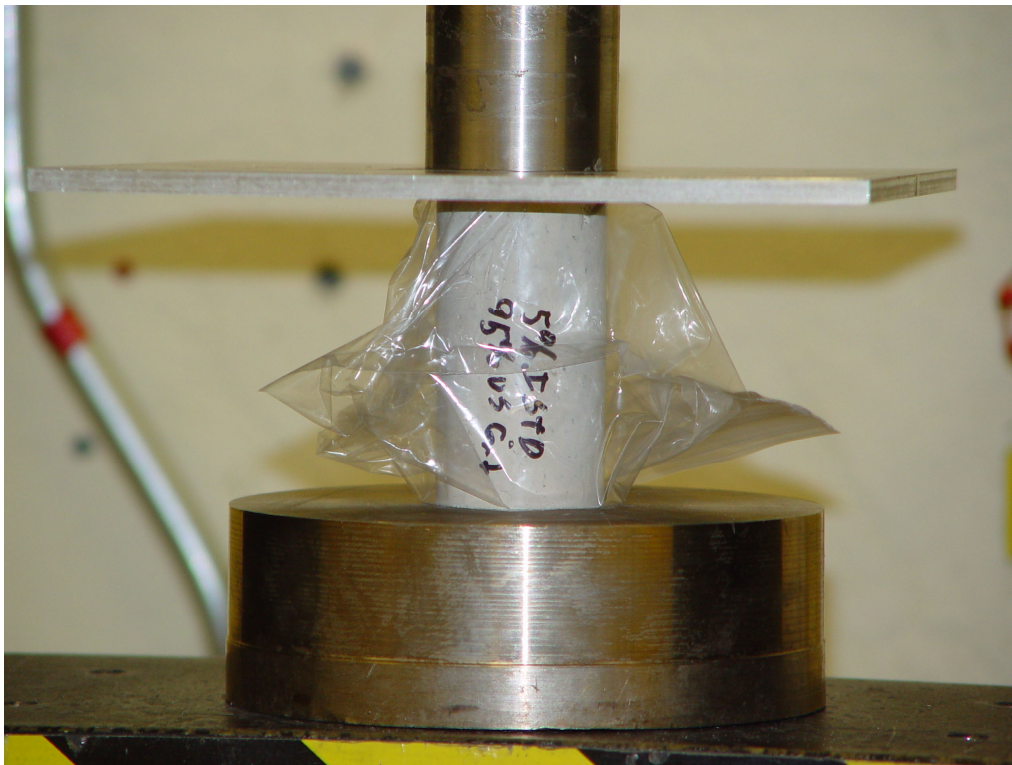


Figure R-2. Photograph of compressive strength of a grouted sample being measured.

R-4. DATA MANAGEMENT, ANALYSIS, AND INTERPRETATION

Compressive-strength data were measured in pounds per square inch, and samples were measured in replicates of five. Averages were determined and error bars presented on figures using 95% confidence intervals.

The data on compressive strength support the areas of risk assessment, risk modeling, and performance evaluation for the Operable Unit 7-13/14 feasibility study. The data quality is used to establish the estimated release rates for contaminants that remain in soil and waste matrices after treatment. The physical property data from these tests are used to predict the long-term physical stability of grouted waste forms.

R-5. RESULTS AND CONCLUSIONS

Mixtures of neat grout, grout with 30 wt% soil, and grout with 50 wt% soil were allowed to cure in constant humidity (98–99%) for at least 30 days. Table R-2 shows results of compressive-strength tests on the three grouts and waste loadings. All of the samples produced compressive strengths in excess of the minimum acceptable value of 250 psi.

Figure R-3 and Table R-3 show compressive-strength values for neat grout and grout mixed with soil. Error bars show the 95% confidence interval. The data show no statistical difference observed (at 95% confidence) among the three grout types (GMENT-12, Portland, and Portland with blast furnace slag) when tested as 0 wt% soil, 30 wt% soil, or 50 wt% soil loading. In general, all of the grouts tested well for compressive strength even at 50 wt% soil loading.

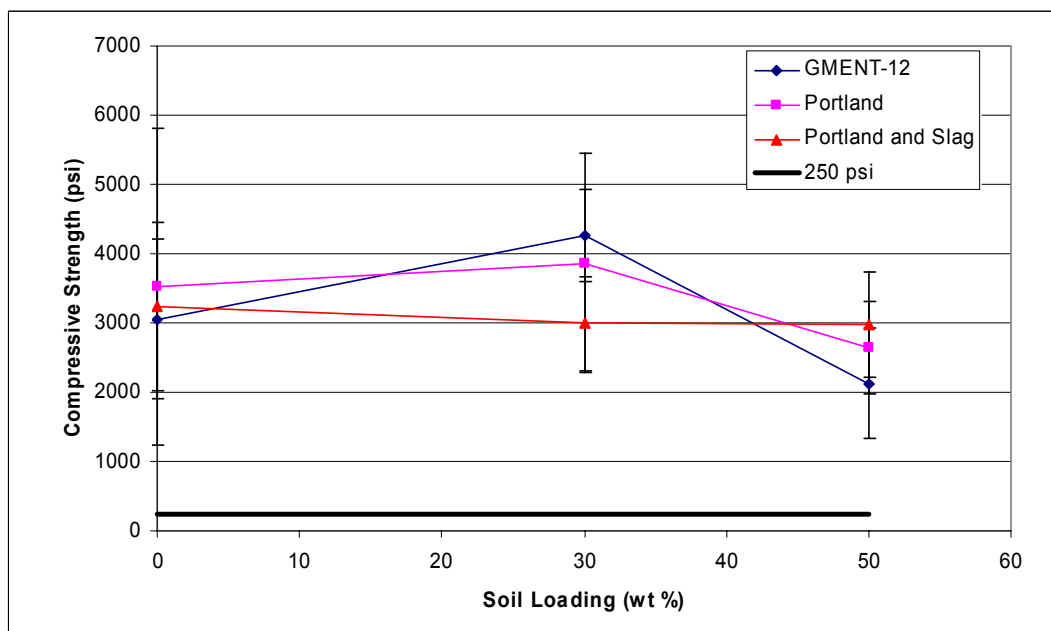


Figure R-3. Compressive strength for grout and grout-soil mixtures.

Table R-2. Compressive strength and splitting tensile strength values for neat grouts.

Test	Grout Product		
	GMMENT-12 (psi)	Portland (psi)	Portland and Blast Furnace Slag (psi)
Compressive strength, Specimen A	2,176	1,569	3,676
Compressive strength, Specimen B	3,252	5,311	1,578
Compressive strength, Specimen C	4,568	4,305	3,127
Compressive strength, Specimen D	2,551	1,543	4,014
Compressive strength, Specimen E	2,734	4,937	3,762
Average compressive strength (psi)	3,056	3,533	3,231
Standard deviation	930	1,840	979
95% confidence interval	1,154	2,285	1,216

Table R-3. Results of individual compressive-strength tests for the interference tolerance testing of grout specimens containing soil from the Idaho National Laboratory Site interference at 30 and 50 wt% loading.

Test	Waste Loading (%)	Grout Compressive Strength		
		GMMENT-12 (psi)	Portland (psi)	Portland and Blast Furnace Slag (psi)
Specimen A	30	3,948	1,953	3,260
Specimen B	30	3,865	4,385	2,812
Specimen C	30	4,014	5,359	3,331
Specimen D	30	5,168	3,445	2,950
Specimen E	30	4,330	4,192	1,857
Specimen F	30	—	—	3,746 ^a
Mean	30	4,265	3,867	2,993
Standard deviation	30	535	1,269	644
95% confidence interval	30	664	1,575	676
Specimen A	50	1,069	323 ^b	1,953
Specimen B	50	2,553	3,113	3,169
Specimen C	50	1,936	2,860	2,903
Specimen D	50	2,519	2,694	3,246
Specimen E	50	2,548	1,880	3,573
Mean	50	2,125	2,637	2,969
Standard deviation	50	646	533	616
95% confidence interval	50	802	662	765

a. Excess sample material was mixed during preparation stage. Since the mixture was prepared, an extra sample was poured and tested.

b. This sample was damaged when it was removed from the mold. The sample was tested, but was not included in the calculations.

R-6. REFERENCES

ASTM C39, 2003, “Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens,” ASTM International.

ASTM D695, 2003, “Standard Test Method for Compressive Properties of Rigid Plastics,” ASTM International.

